

AD-A092 964

ALBERTA UNIV EDMONTON DEPT OF CHEMISTRY F/G 7/4
SIMULATION OF ELECTROCHEMICAL PROCESSES BY ORTHOGONAL COLLOCATI--ETC(U)
DEC 80 B S PONS N00014-80-6-0107

UNCLASSIFIED

TR-3

NL

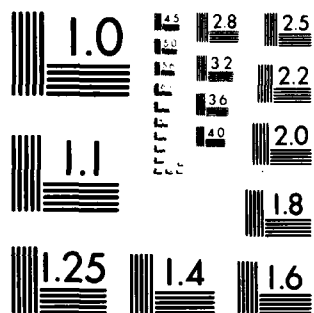
END

DATE

FORMED

1 81

DTIC



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS 1963 A

AD A092964

LEVEL II

(12)

OFFICE OF NAVAL RESEARCH

Contract N00014-80-0107

Task No. NR 359-718

9 TECHNICAL REPORT NO. 3

14 7 F 31

Simulation of Electrochemical Processes by
Orthogonal Collocation. Spherical Electrode Geometry.

by

B. Stanley Pons

Prepared for Publication

in the

Canadian Journal of Chemistry

DTIC
ELECTE
DEC 17 1980
S D
E

University of Alberta
Department of Chemistry
Edmonton, Alberta

December 8, 1980

Reproduction in whole or in part is permitted for
any purpose of the United States Government

This document has been approved for public release
and sale; its distribution is unlimited

DOC FILE COPY

80 12 15 1 66

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER 3	2. GOVT ACCESSION NO. AD-A092964	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Simulation of Electrochemical Processes by Orthogonal Collocation. Spherical Electrode Geometry		5. TYPE OF REPORT & PERIOD COVERED Technical Report # 3
7. AUTHOR(s) B. Stanley Pons		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry University of Alberta Edmonton, Alberta, Canada T6G 2G2		8. CONTRACT OR GRANT NUMBER(s) N00014-80-G-0107
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Chemistry Program - Chemistry Code 472 Arlington, Virginia 22217		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 359-7.1.8/7-22-80
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE December 8, 1980
		13. NUMBER OF PAGES 32
		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) This document has been approved for public release and sale; its distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Digital Simulation, Orthogonal Collocation, Electrochemical Simulation, Electrochemical Kinetics		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Discretization formulas for the digital simulation of the diffusional processes associated with a variety of electrochemical processes at a spherical electrode are given. The formulas are based on orthogonal collocation techniques. Several mechanisms are represented, and the technique is demonstrated for chromoamperometry, chronopotentiometry, and cyclic voltammetry.		

DD FORM 1473
1 JAN 73

EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-11-014-6601

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

Accession For	
NTIS GRA&I	<input checked="" type="checkbox"/>
DDC TAB	
Unannounced	
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or special
A	

SIMULATION OF ELECTROCHEMICAL PROCESSES BY
ORTHOGONAL COLLOCATION. SPHERICAL ELECTRODE GEOMETRY

B. Stanley Pons
Department of Chemistry
University of Alberta
Edmonton, Alberta, Canada
T6G 2G2

This paper is dedicated to Professor W.E. Harris on the
occasion of his retirement from the University of Alberta.

ABSTRACT

Discretization formulas for the digital simulation of the diffusional processes associated with a variety of electrochemical processes at a spherical electrode are given. The formulas are based on orthogonal collocation techniques. Several mechanisms are represented, and the technique is demonstrated for chronoamperometry, chronopotentiometry, and cyclic voltammetry.

Orthogonal collocation techniques for the simulation of second order partial differential equations have been demonstrated for a variety of problems in electrochemistry [1-7], chemical engineering [8-11], differential scanning calorimetry [12], and other fields [13]. The advantages over other methods have been described, but noteworthy is generally increased accuracy for decreased computational effort [1-7].

In electrochemical diffusion problems, the algorithms needed to compute concentration profiles, chronopotentiograms, chronoamperometric responses, spectrophotometric responses of individual species, cyclic voltammograms, and chronocoulometric responses, all to planar electrode configurations, have been given. This paper deals with some of the same experiments applied to a common configuration, the static spherical electrode (Figure 1).

The programs for solving the equations described herein have been given [7]. Basically, the orthogonal collocation technique is implemented by the following steps:

1. Make the Fick's laws equations suitably dimensionless.
2. Discretize the resulting equations at the roots (zeros) of an orthogonal polynomial of suitable symmetry. The resulting set of equations are now first order ordinary differential equations.
3. Integrate the set of simultaneous differential equations to obtain the set of concentration profiles with respect to distance from the electrode surface and with time.
4. Use these concentrations in the suitably discretized equations to obtain the desired electrochemical parameter (current, absorbance, etc.).

Chronoamperometry

We will only consider diffusion on the solution side of the electrode-solution interface. For a chronoamperometric experiment on the simple charge transfer mechanism at a spherical electrode



we have the following imposed conditions:

$$\begin{aligned} [A]_{R,0} &= [A]_{\infty,T} = [A^\circ] \\ [A]_{r_0,T} &= [B]_{\infty,T} = [B]_{R,0} = 0 \\ \left(\frac{\delta[A]}{\delta R} \right)_{R=r_0} &= - \left(\frac{\delta[B]}{\delta R} \right)_{R=r_0} \end{aligned} \quad (2)$$

where R is the distance parameter (radial) from the center of the spherical electrode and r_0 = the radius of the electrode. Since interpolation methods using orthogonal polynomials are simpler to use in a $[0,1]$ interval, we will define M as some distance in the R direction such that no diffusion effects are experienced there during the time frame of the experiment. The differential equation for the A species is:

$$\frac{\delta[A]}{\delta T} = \frac{D_A \delta^2[A]}{\delta R^2} + \frac{2D_A}{R} \frac{\delta[A]}{\delta R} \quad (3)$$

For dimensionless variables, we choose

$$c_A = \frac{[A]}{[A^\circ]} \quad t = \frac{DT}{(M-r_0)^2} \quad r = \frac{R-r_0}{M-r_0} \quad (4)$$

We note then that

$$dT = \frac{(M-r_0)^2}{D_A} dt, \text{ and} \quad (5)$$

$$dR = (M-r_0) dr$$

Substitution of the new variables (4) into (3) gives

$$\frac{D_A [A^\circ] \delta c_A}{(M-r_0)^2 \delta t} = \frac{D_A [A^\circ] \delta^2 c_A}{(M-r_0)^2 \delta r^2} + \left(\frac{2D_A}{(M-r_0)r+r_0} \right) \frac{[A^\circ] \delta c_A}{(M-r_0) \delta r} \quad (6)$$

which, after simplification, leads to

$$\frac{\delta c_A}{\delta t} = \frac{\delta^2 c_A}{\delta r^2} + \frac{2}{r + \beta} \frac{\delta c_A}{\delta r} \quad (7)$$

where

$$\beta = \frac{r_0}{M-r_0}$$

The general spatial derivatives in terms of their polynomial interpolation coefficients [1] are given by

$$\left(\frac{dQ}{dx} \right)_{x=x_i} = \sum_{j=1}^{N+2} A_{i,j} Q(x_j, t) \quad (8a)$$

$$\left(\frac{d^2 Q}{dx^2} \right)_{x=x_i} = \sum_{j=1}^{N+2} B_{i,j} Q(x_j, t) \quad (8b)$$

where N is the order of the approximation polynomial chosen, the x_i represents the roots of that polynomial collocation points, and the A_{ij} and B_{ij} are given by [10]

$$[A_{ij}] = \begin{bmatrix} dx_1^0/dx & dx_1^1/dx & \text{-----} & dx_1^{N+2}/dx \\ dx_2^0/dx & & & \\ \vdots & & & \\ dx_{N+2}^0/dx & & \text{-----} & dx_{N+2}^{N+2}/dx \end{bmatrix} \begin{bmatrix} S \\ \vdots \\ S \end{bmatrix}^{-1} \quad (9)$$

and

$$[B_{ij}] = \begin{bmatrix} d^2x_1^0/dx^2 & d^2x_1^1/dx^2 & \text{-----} & d^2x_1^{N+2}/dx^2 \\ d^2x_2^0/dx^2 & & & \\ \vdots & & & \\ d^2x_{N+2}^0/dx^2 & & \text{-----} & d^2x_{N+2}^{N+2}/dx^2 \end{bmatrix} \begin{bmatrix} S \\ \vdots \\ S \end{bmatrix}^{-1} \quad (10)$$

The matrix [S] is given by

$$[S] = \begin{bmatrix} x_0^0 & x_0^1 & \text{----} & x_0^{N+2} \\ x_1^0 & & \text{----} & \\ \vdots & & & \\ x_{N+2}^0 & & \text{----} & x_{N+2}^{N+2} \end{bmatrix} \quad (11)$$

The algorithms for finding the roots of any orthogonal polynomial and the corresponding $[A_{ij}]$ and $[B_{ij}]$ matrices have been given previously [9]. The $N+2$ terms arise because $X=0$ and $X=1$ are included as roots to the orthogonal polynomial. The concentration profile will be evaluated at the collocation point, i.e. at concentric spheres surrounding the spherical electrode. Each sphere has radius $r=X_1, X_2, X_3$, etc., i.e. at the collocation points.

Equation (7) is thus written in terms of (8a) and (8b) at the discrete points X_i :

$$\left. \frac{dc_A}{dt} \right|_{r_i=X_i} = \sum_{j=1}^{N+2} B_{ij} c_A(r_j, t) + \frac{2}{r_i^{1+\beta}} \sum_{j=1}^{N+2} A_{ij} c_A(r_j, t) \quad (12)$$

Thus we have $N+2$ simultaneous first order differential equations to solve for the $N+2$ $c_A(r_j, t)$ unknowns. Any one of several methods may be used for solving this system of equations [1,4,9].

Inserting the boundary conditions (2) further defines the electrochemical method used, and reduces the number of equations from $N+2$ to N . This is done by first expanding equation (12) partially, exposing the boundary points at $r_1 = X_1 = 0$ and $r_{N+2} = X_{N+2} = 1$:

$$\left. \frac{dc_A}{dt} \right|_{r_i = X_i} = B_{i,1} c_A(0,t) + B_{i,N+2} c_A(1,t) + \sum_{j=2}^{N+1} B_{ij} c_A(r_j, t) + \frac{2}{r_i + \beta} \left[A_{i,1} c_A(0,t) + A_{i,N+2} c_A(1,t) + \sum_{j=2}^{N+1} A_{ij} c_A(r_j, t) \right] \quad (13)$$

We have from the original boundary conditions (2) that $c_A(0,t) = 0$ and $c_A(1,t) = 1$, so that (14) becomes

$$\left. \frac{dc_A}{dt} \right|_{r_i = X_i} = B_{i,N+2} + \sum_{j=2}^{N+1} B_{ij} c_A(r_j, t) + \frac{2}{r_i + \beta} \left[A_{i,N+2} + \sum_{j=2}^{N+1} A_{ij} c_A(r_j, t) \right] \quad (14)$$

So we have one equation to solve at each of the N interior collocation points X_i , $i = 2, \dots, N+1$ for the N unknown $c_A(r_j, t)$.

The concentration profile for the B species is derived similarly, and leads to identically the same result as equation (12):

$$\left. \frac{dc_B}{dt} \right|_{r_i = X_i} = \sum_{j=1}^{N+2} B_{ij} c_B(r_j, t) + \frac{2}{r_i + \beta} \sum_{j=1}^{N+2} A_{ij} c_B(r_j, t) \quad (15)$$

Partial expansion leads again to equation (13) with $c_B(r_j, t)$ substituted for the $c_A(r_j, t)$. However, even though it is true that one boundary

condition, $c_B(i,t) = 1$ may be immediately substituted, the other boundary condition $c_B(0,t)$ is not known explicitly. This problem is easily resolved in collocation methods. We observe that the flux relation

$$D_A \left. \frac{dc_A}{dr} \right|_{r_1=x_1=0} = -D_B \left. \frac{dc_A}{dr} \right|_{r_1=x_1=0} \quad (16)$$

We will let $D_A = D_B$ here for convenience even though it presents no problem in setting up the equations if we do not [1,4]. The flux relation is replaced by equation (8a) on each side:

$$\sum_{i=1}^{N+2} A_{1,j} c_A(r_j, t) = - \sum_{i=1}^{N+2} A_{1,j} c_B(r_j, t) \quad (17)$$

Partially expanding so that known conditions may be inserted, we have

$$\begin{aligned} A_{1,1} c_A(0,t) + A_{1,N+2} c_A(1,t) + \sum_{i=2}^{N+1} A_{1,j} c_A(r_j, t) = \\ - [A_{1,1} c_B(r_j, t) + A_{1,N+2} c_B(1,t) + \sum_{i=2}^{N+1} A_{1,j} c_B(r_j, t)] \end{aligned} \quad (18)$$

Inserting known quantities, we deduce

$$A_{1,N+2} + \sum_{i=1}^{N+1} A_{1,j} c_A(r_j, t) = - [A_{1,1} c_B(0,t) + \sum_{i=2}^{N+1} A_{1,j} c_B(r_j, t)] \quad (19)$$

Solving for our unknown boundary condition,

$$c_B(0,t) = U + \sum_{i=2}^{N+1} C_{1,j} (c_A(r_j, t) + c_B(r_j, t)) \quad (20)$$

where

$$U = \frac{A_{1,N+2}}{A_{1,1}}, \text{ and}$$

$$C_{1,j} = \frac{A_{1,j}}{A_{1,1}}$$

We can now substitute this explicit value for $c_B(0,t)$ in equation (15), along with $c_B(1,t) = 0$ to obtain the equation necessary to represent the concentration profiles for B:

$$\left. \frac{dc_B}{dt} \right|_{r_j=X_i} = V_i + \sum_{j=2}^{N+1} D_{ij} c_A(r_j, t) + \sum_{j=2}^{N+1} E_{ij} c_B(r_j, t) \quad (21)$$

where

$$V_i = B_{i,1}T + \frac{2A_{i,1}U}{r_i + \beta}$$

$$D_{ij} = C_{i,j} \left[B_{i,1} + \frac{2A_{i,1}}{r_i + \beta} \right]$$

$$E_{ij} = B_{ij} + C_{i,j} \left[G_{i,1} + \frac{2A_{i,1}}{r_i + \beta} \right] + \frac{2A_{i,j}}{r_i + \beta}$$

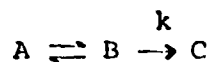
Again we have N equations in the N unknown $c_B(r_j, t)$ to solve simultaneously.

Table 1 compares results obtained for the current obtained by equation (33) and the analytic solution for this case, which is

$$i = \frac{nFAD_A^{1/2}[A^\circ]}{\pi^{1/2}T^{1/2}} + \frac{nFAD_A[A^\circ]}{r_0} \quad (22)$$

We use, by example, $D_A = 1. \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, $[A^\circ] = 10^{-6} \text{ moles cm}^{-3}$, $A = \pi r_0^2$, $r_0 = 0.1 \text{ cm}$, and $n = 1$. β for the example was 10^4 .

For the mechanism,



the profile for the A species is the same as equation (14). The B species has a different profile due to loss of material through the chemical reaction, i.e.

$$\frac{\delta[B]}{\delta t} = D_B \frac{\delta^2[B]}{\delta R^2} + \frac{2D_B}{R} \frac{\delta[B]}{\delta R} - k[B] \quad (23)$$

After discretization to the collocation points and insertion of the dimensionless variables (4), we have

$$\left. \frac{dc_B}{dt} \right|_{r_i=x_i} = \sum_{j=1}^{N+2} B_{i,j} c_B(r_j, t) + \frac{2}{r_i+\beta} \sum_{j=1}^{N+2} A_{i,j} c_B(r_j, t) - \alpha c_B(r_i, t) \quad (24)$$

where

$$\alpha = \frac{k(M-r_0)^2}{D_B}$$

Continuing precisely as for the simple electron transfer case, except with the addition of this last chemical kinetic term, we find that

$$\left. \frac{dc_B}{dt} \right|_{r_i=x_i} = V_i + \sum_{j=2}^{N+1} D_{ij} c_A(r_j, t) + \sum_{j=2}^{N+1} E_{ij} c_B(r_j, t) - \alpha c_B(r_j, t) \quad (25)$$

For the catalytic mechanism



both the A and B profiles are modified by the presence of the chemical reaction. The differential equations are

$$\begin{aligned} \frac{\delta[A]}{\delta t} &= D_A \frac{\delta^2[A]}{\delta R^2} + \frac{2D_A}{R} \frac{\delta[A]}{\delta R} + k[B] \\ \frac{\delta[B]}{\delta t} &= D_B \frac{\delta^2[B]}{\delta R^2} + \frac{2D_B}{R} \frac{\delta[B]}{\delta R} - k[B] \end{aligned} \quad (27)$$

The boundary conditions are exactly as the previous cases, so that discretization is the same. We find that

$$\left. \frac{dc_A}{dt} \right|_{r_i=x_i} = B_{i,N+2} + \sum_{j=2}^{N+1} B_{ij} c_A(r_j, t) + \frac{2}{r_i + \beta} [A_{i,N+2} + \sum_{j=2}^{N+1} A_{ij} c_A(r_j, t)] + \alpha c_B(r_j, t) \quad (28)$$

$$\left. \frac{dc_B}{dt} \right|_{r_i=x_i} = \sum_{j=2}^{N+1} D_{ij} c_A(r_j, t) + \sum_{j=2}^{N+1} E_{ij} c_B(r_j, t) - \alpha c_B(r_j, t) \quad (29)$$

again letting $D_A = D_B$.

To calculate the current at any time for the mechanisms listed above under the chronoamperometric experiment, we note the following:

$$i = nFAD_A \left(\frac{d[A]}{dR} \right)_{R=0} \quad (30)$$

where A is the electrode surface area and F is the Faraday constant. The flux term is converted to dimensionless terms by insertion of the newly defined variables (4).

$$i = \frac{nFAD[A^0]}{M-r_0} \left(\frac{dc_A}{dr} \right)_{r_1=x_1=0} \quad (31)$$

The flux term may then be discretized to

$$i = \frac{nFAD[A^0]}{M-r_0} [A_{1,1} c_A(0, t) + A_{1,N+2} c_A(1, t) + \sum_{j=2}^{N+1} A_{1,j} c_A(r_j, t)] \quad (32)$$

or

$$i = \frac{nFAD[A^0]}{M-r_0} [A_{1,N+2} + \sum_{j=2}^{N+1} A_{1,j} c_A(r_j, t)] \quad (33)$$

after insertion of the known values of $c_A(0, t)$ and $c_A(1, t)$.

So the current i may be calculated at any time

$$T = \frac{(M-r_0)^2 t}{D} \text{ by insertion of the calculated concentrations from}$$

equations (14) or (28) into equation (33). If there are additional electroactive species in the mechanism, their contribution is simply added into equation (33), since generally,

$$i = \frac{nFAD[A^0]}{M-r_0} \sum_{n=1}^m \left(\frac{dc_n}{dr} \right)_{r=X_1=0} \quad (34)$$

where m is the total number of electroactive species.

The charge or spectroelectrochemical absorbance can be calculated by use of Gaussian quadrature weights [4,9,10] for the integration of the current in time or the concentration profiles in time.

Cyclic Voltammetric Response

Several modifications have to be made to the method of Speiser and Rieker [6] to develop the cyclic voltammetric responses for the spherical electrode. We define new dimensionless time and distance variables

$$t = \frac{DTa}{(M-r_0)^2} \quad (35)$$

and

$$r = \frac{(R-r_0)a^{1/2}}{M-r_0}$$

where

$$a = nFv/R'T'$$

with v = the potential sweep rate in volts s^{-1} , R' the gas constant, and T' the temperature. Thus,

$$dT = \frac{(M-r_0)^2 dt}{aD}$$

and

$$dR = \frac{(M-r_0)dr}{a^{1/2}} \quad (36)$$

For the simple electron transfer reaction (1), the differential equation (6) becomes

$$\frac{aD[A^\circ]\delta c_A}{(M-r_0)^2\delta t} = \frac{aD[A^\circ]\delta^2 c_A}{(M-r_0)^2\delta r^2} + \frac{2D[A^\circ]}{((M-r_0)r+r_0)(M-r_0)} \frac{\delta c_A}{\delta r} \quad (37)$$

which simplifies to

$$\frac{\delta c_A}{\delta t} = \frac{\delta^2 c_A}{\delta r^2} + \frac{2a^{1/2}}{r+\beta} \frac{\delta c_A}{\delta r} \quad (38)$$

The derivation now proceeds as described by Speiser and Rieker [6].

The cyclic voltammetric boundary conditions are

$$\begin{aligned} [A]_{R;0} &= [A]_{\infty,t} = [A^\circ] \\ [B]_{R;0} &= [B]_{\infty,t} = 0 \end{aligned} \quad (39)$$

$$\frac{\delta[A]}{\delta R} \bigg|_{R=0} = -\frac{\delta[A]}{\delta R} \bigg|_{R=0}$$

$$\frac{[A]_{0,T}}{[B]_{0,T}} = \exp[nF/R'T'(E_{A/B}^\ominus - E)] = \theta_{A/B} S_\lambda(t)$$

Inserting the potential sweep rate (14) v , we have

$$\begin{aligned} \theta_{A/B} &= \exp[nF/R'T'(E_{A/B}^\ominus - E_{\text{START}})] \\ S_\lambda(T) &= \begin{cases} \exp(-nFvT/R'T') = \exp(-aT) & \text{for } T \leq T_\lambda \\ \exp(at - 2aT_\lambda) & \text{for } T_\lambda \leq T \leq 2T \end{cases} \end{aligned} \quad (40)$$

where T is the time when the forward potential sweep is reversed.

We convert equations (39) to dimensionless form normalized to t and M :

$$\begin{aligned}
 c_A(r,0) &= c_A(1,t) = 1 \\
 c_B(r,0) &= c_B(1,t) = 0 \\
 \left(\frac{\delta c_A}{\delta r}\right)_{r=0} &= \left(\frac{-\delta c_B}{\delta r}\right)_{r=0} \\
 \frac{c_A(0,t)}{c_B(0,t)} &= \theta_{A/B} S_\lambda(t)
 \end{aligned} \tag{41}$$

Discretizing using equations (8a) and (8b) on (38), we have

$$\left. \frac{dc_A}{dt} \right|_{r_i=x_i} = \sum_{j=1}^{N+2} B_{ij} c_A(r_j, t) + \frac{2a^{1/2}}{r_i + \beta} \sum_{j=1}^{N+2} A_{ij} c_A(r_j, t) \tag{42}$$

or after partial expansion

$$\begin{aligned}
 \left. \frac{dc_A}{dt} \right|_{r_i=x_i} &= B_{i,1} c_A(0,t) + B_{i,N+2} c_A(1,t) + \sum_{j=2}^{N+1} B_{ij} c_A(r_j, t) + \\
 &\quad \frac{2a^{1/2}}{r_i + \beta} [A_{i,1} c_A(0,t) + A_{i,N+2} c_A(1,t) + \sum_{j=2}^{N+1} A_{ij} c_A(r_j, t)]
 \end{aligned} \tag{43}$$

Inserting the explicit boundary conditions, we have

$$\begin{aligned}
 \left. \frac{dc_A}{dt} \right|_{r_j=x_j} &= B_{i,1} c_A(0,t) + B_{i,N+2} c_A(1,t) + \sum_{j=2}^{N+1} B_{ij} c_A(r_j, t) + \frac{2a^{1/2}}{r_i + \beta} [A_{i,1} c_A(0,t) \\
 &\quad + A_{i,N+2} c_A(1,t) + \sum_{j=2}^{N+1} A_{ij} c_A(r_j, t)]
 \end{aligned} \tag{44}$$

Identical treatment for the B species yields

$$\left. \frac{dc_B}{dt} \right|_{r_i=x_i} = B_{i,1} c_B(0,t) + \sum_{j=2}^{N+1} B_{ij} c_B(r_j,t) + \frac{2a^{1/2}}{r_i + \beta} [A_{i,1} c_B(0,t) + \sum_{j=2}^{N+1} A_{ij} c_B(r_j,t)] \quad (45)$$

We discretize the flux relation in (41) to get an equation relating $c_A(0,t)$ and $c_B(0,t)$, presently implicit boundary conditions.

$$\sum_{j=1}^{N+2} A_{k,j} c_A(r_j,t) = - \sum_{j=1}^{N+2} A_{i,j} c_B(r_j,t) \quad (46)$$

Rieker and Speiser [6] showed that after expansion of equation (46), one may then substitute in equation (44) and arrive at the following result giving the time (potential) dependence of $c_A(0,t)$ and $c_B(0,t)$:

$$c_A(0,t) = - \frac{\theta_{A/B} S_\lambda(t)}{A_{1,1} [1 + \theta_{A/B} S_\lambda(t)]} A_{1,N+2} + \sum_{j=2}^{N+1} A_{1,j} (c_A(r_j,t) + c_B(r_j,t)) \quad (47)$$

$$c_B(0,t) = - \frac{1}{A_{1,1} [1 + \theta_{A/B} S_\lambda(t)]} A_{1,N+2} + \sum_{j=2}^{N+1} A_{1,j} (c_A(r_j,t) + c_B(r_j,t))$$

Inserting these time dependent boundary conditions into the discretized equations (44) and (45) yield the $2N$ simultaneous first order differential equations necessary to solve for the concentration profiles in time:

$$\left. \frac{dc_A}{dt} \right|_{r_i=x_i} = W_i + \sum_{j=2}^{N+1} F_{ij} c_A(r_j,t) + \sum_{j=2}^{N+1} G_{ij} c_B(r_j,t)$$

$$\left. \frac{dc_B}{dt} \right|_{r_i=x_i} = x_i + \sum_{j=2}^{N+1} H_{ij} c_A(r_j, t) + \sum_{j=2}^{N+1} I_{ij} c_B(r_j, t)$$

with

$$W_i = - \frac{\theta_{A/B} S_\lambda(t)}{A_{1,1} [1 + \theta_{A/B} S_\lambda(t)]} [B_{i,1} A_{1,N+2} + \frac{2a^{1/2}}{r_i + \beta} A_{i,1} A_{1,N+2}] +$$

$$B_{i,N+2} + \frac{2a^{1/2}}{r_i + \beta} A_{i,N+2}$$

$$F_{ij} = B_{ij} + \frac{2a^{1/2}}{r_i + \beta} A_{ij} - \frac{2a^{1/2} A_{i,1} A_{1,j} \theta_{A/B} S_\lambda(t)}{(r_i + \beta) A_{1,1} [1 + \theta_{A/B} S_\lambda(t)]} -$$

$$\frac{B_{i,1} A_{1,j} \theta_{A/B} S_\lambda(t)}{A_{1,1} [1 - \theta_{A/B} S_\lambda(t)]}$$

$$G_{ij} = - \frac{\theta_{A/B} S_\lambda(t)}{A_{1,1} [1 + \theta_{A/B} S_\lambda(t)]} [B_{i,1} A_{1,j} + \frac{2a^{1/2} A_{i,1} A_{1,j}}{(r_i + \beta)}]$$

$$W_i = - \frac{1}{A_{1,1} [1 + \theta_{A/B} S_\lambda(t)]} [B_{i,1} A_{1,N+2} + \frac{2a^{1/2}}{r_i + \beta} A_{i,1} A_{1,N+2}]$$

$$H_{ij} = - \frac{1}{A_{1,1} [1 + \theta_{A/B} S_\lambda(t)]} [B_{i,1} A_{1,j} - \frac{2a^{1/2} A_{i,1} A_{1,j}}{r_i + \beta}]$$

$$I_{ij} = B_{ij} + \frac{2a^{1/2}}{r_i + \beta} A_{ij} - \frac{2a^{1/2} A_{i,1} A_{1,j}}{(r_i + \beta) A_{1,1} [1 + \theta_{A/B} S_\lambda(t)]} -$$

$$\frac{B_{i,1} A_{1,j}}{A_{1,1} [1 + \theta_{A/B} S_\lambda(t)]}$$

The 2N equations (48) are solved simultaneously as before to find the $c_A(r_j, t)$ and $c_B(r_j, t)$.

The current response is represented similar to the chronoamperometric case:

$$i = nFAD_A \left(\frac{\delta [A]}{\delta R} \right)_{R=0}$$

or in the dimensionless space

$$i = \frac{nFAD_A [A^\circ] a^{1/2}}{(M-r_0)} \left(\frac{dc_A}{dr} \right)_{r_1=x_1=0} \quad (50)$$

Discretizing the flux and inserting the boundary conditions leads to (6)

$$\left. \frac{dc_A}{dr} \right|_{r_1=x_1} = \frac{1}{1+\theta_{A/B} S_\lambda(t)} [A_{1,N+2} + \sum_{j=2}^{N+1} A_{1,j} c_A(r_j, t) - \theta_{A/B} S_\lambda(t) \sum_{j=2}^{N+1} A_{1,j} c_B(r_j, t)] \quad (51)$$

So that

$$i = \frac{nFAD_A [A^\circ] a^{1/2}}{(M-r_0)} \left[\frac{1}{1+\theta_{A/B} S_\lambda(t)} [A_{1,N+2} + \sum_{j=2}^{N+1} A_{1,j} c_A(r_j, t) - \theta_{A/B} S_\lambda(t) \sum_{j=2}^{N+1} A_{1,j} c_B(r_j, t)] \right] \quad (52)$$

The concentrations $c_A(r_i, t)$ and $c_B(r_i, t)$ found at each time $T = (M-r_0)^2 t / aD$ are used in equation (52) to determine the current as a function of time and hence potential by the relation

$$E = \begin{cases} E_{\text{START}} + \frac{(M-r_0)^2 t R' T'}{nFD} & t \leq t \\ E_{\text{START}} + 2vt_\lambda - \frac{(M-r_0)^2 t R' T'}{nFD} & t \leq t \leq 2t \end{cases} \quad (53)$$

where t is the dimensionless potential sweep reversal time

$$t_\lambda = \frac{aDT_\lambda}{(M-r_0)^2}$$

Chronopotentiometry

The chronopotentiometric case for planar electrodes was described in a previous paper. For a chronopotentiometric response to the simple reversible charge transfer reaction, we must consider the following conditions:

$$[A]_{r,0} = [A]_{\infty,T} = [A^\circ]$$

$$[B]_{r,0} = [B]_{\infty,T} = 0 \quad (54)$$

$$E + E_{A/B}^\circ - \frac{R'T'}{nF} \ln[B]_{r_0}$$

$$\left(\frac{\delta[A]}{\delta R}\right)_{r_0} = - \left(\frac{\delta[B]}{\delta R}\right)_{r_0} \quad (55)$$

$$i = nFAD_A \left(\frac{\delta[A]}{\delta r}\right)_{R=r_0} = \text{Constant}$$

The new dimensionless parameters are

$$t = T/\tau \quad r = \frac{R-r_0}{M-r_0} \quad (56)$$

with τ the transition time of the experiment. Insertion of these values into the differential equation (3) and simplification yields

$$\frac{\delta c_A}{\delta t} = \alpha \frac{\delta^2 c_A}{\delta r^2} + \frac{2\alpha}{r+\beta} \frac{\delta c_A}{\delta r} \quad (57)$$

where

$$\alpha = \frac{D\tau}{(M-r_0)^2}$$

The conditions (54-55) in dimensionless form become

$$c_A(r,0) = c_A(1,t) = 1$$

$$c_B(r,0) = c_B(1,t) = 0$$

$$\left(\frac{\delta c_A}{\delta r}\right)_{r_0} = -\left(\frac{\delta c_B}{\delta r}\right)_{r_0}$$

$$i = \frac{nFAD[A^\circ]}{(M-r_0)} \left(\frac{dc_A}{dr}\right)_{r_0} = \frac{nFAD^{1/2}\alpha^{1/2}}{\tau^{1/2}} \frac{nFAD^{1/2}[A^\circ]\alpha^{1/2}}{\tau^{1/2}} \left(\frac{dc_A}{dr}\right)_{r_0}$$

The flux relation at the electrode is given from (8a)

$$\left(\frac{dc_A}{dr}\right)_{r_0} = \sum_{j=1}^{N+2} A_{1,j} c_A(r_j, t)$$

$$\left(\frac{dc_B}{dr}\right)_{r_0} = \sum_{j=1}^{N+2} A_{1,j} c_B(r_j, t)$$

Upon entering the known boundary conditions and expanding, and then substituting these into (59) we have

$$c_A(0,t) = Q - \sum_{j=2}^{N+1} a_j c_A(r_j, t)$$

$$c_B(0,t) = R - \sum_{j=2}^{N+1} a_j c_B(r_j, t)$$

with

$$Q = \frac{1}{A_{1,1}} \left[\frac{i_1^{1/2}}{nFA[A^\circ]D^{1/2}\alpha^{1/2}} - A_{1,N+2} \right]$$

$$R = \frac{1}{A_{1,1}} \left[\frac{i_1^{1/2}}{nFA[A^\circ]D^{1/2}\alpha^{1/2}} \right]$$

$$a_j = \frac{A_{1,j}}{A_{1,1}}$$

The discretized equations for A and B are thus

$$\left. \frac{dc_A}{dt} \right|_{r_i=x_i} = \sum_{j=1}^{N+2} B_{ij} c_A(r_j, t) + \frac{2\alpha}{r_i+\beta} \sum_{j=1}^{N+2} A_{ij} c_A(r_j, t) \quad (62)$$

$$\left. \frac{dc_B}{dt} \right|_{r_i=x_i} = \sum_{j=1}^{N+2} B_{ij} c_B(r_j, t) + \frac{2\alpha}{r_i+\beta} \sum_{j=1}^{N+2} A_{ij} c_B(r_j, t)$$

The known boundary conditions from equations (58) and (61) are entered, and we have

$$\left. \frac{dc_A}{dt} \right|_{r_i=x_i} = \alpha Q'_i + \alpha \sum_{j=2}^{N+1} b_{ij} c_A(r_j, t) \quad (63)$$

$$\left. \frac{dc_B}{dt} \right|_{r_i=x_i} = \alpha R'_i + \alpha \sum_{j=2}^{N+1} b_{ij} c_B(r_j, t)$$

where

$$Q'_i = B_{i,1}Q + B_{i,N+2} + \frac{2\alpha}{r_i+\beta} (A_{i,1}Q + A_{i,N+2})$$

$$R'_i = B_{i,1}R + \frac{2A_{i,1}R}{r_i+\beta}$$

$$b_{ij} = -B_{i,1}a_j + B_{ij} = \frac{2}{r_i+\beta} (A_{i,1}a_j - A_{ij})$$

The usual display of the response is given by

$$E = E_{A/B}^{\ominus} - \frac{R'T'}{nF} \ln \left(\frac{c_B(0,t)}{c_A(0,t)} \right) \quad (64)$$

where the two concentration terms in brackets are found from equation (61). The concentration terms in (61) are found by integration of the simultaneous equation (63) by the methods described [1,4,5,9] previously.

REFERENCES

1. L.F. Whiting and P.W. Carr, J. Electroanal. Chem. 81, 1 (1977).
2. A. Bewick, J. Mellor, and B.S. Pons, Electrochimica Acta 23, 77 (1978).
3. A. Bewick, J. Mellor, and B.S. Pons, Electrochimica Acta 25, 931 (1980).
4. B.S. Pons and P.P. Schmidt, Electrochimica Acta 25, 987 (1980).
5. B. S. Pons, Electrochimica Acta, in press.
6. B. Speiser and A. Rieker, J. Electroanal. Chem. 102, 1 (1979).
7. B. Speiser, J. Electroanal. Chem. 110, 69 (1980).
8. J. Villadsen, "Selected Approximation Methods for Chemical Engineering Problems", Reproset, Copenhagen, 1970.
9. J. Villadsen and M.L. Michelsen, "Solution of Differential Equation Models by Polynomial Approximation", Prentice Hall, Englewood Cliffs, 1978.
10. J. Villadsen and W.E. Stewart, Chem. Eng. Sci. 22, 1483 (1967).
11. J. Villadsen and J.P. Sorenson, Chem. Eng. Sci. 24, 1337 (1969).
12. L.F. Whiting and P.W. Carr, Anal. Chem. 50, 1997 (1978).
13. See references by B.A. Finlayson in Richard Bellman (ed), Mathematics in Science and Engineering, Vol. 87, Academic Press, New York, 1972.
14. R.S. Nicholson and I. Shain, Anal. Chem. 36, 706 (1964).

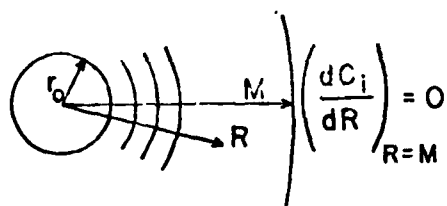
Table 1

<u>Time, sec</u>	<u>i_{exact}, ma</u>	<u>i_{sinulated}, ma</u>
1×10^{-5}	1.7104	1.7104
1×10^{-4}	0.5411	0.5412
1×10^{-3}	0.1713	0.1712
1×10^{-2}	0.0054	0.0054
1×10^{-1}	0.0017	0.0017
1×10^0	0.0001	0.0001

Comparison of exact and simulated currents for the simple change transfer chronoamperometric experiment. (N = 6 collocation points.) See text for parameters.

FIGURE CAPTION

Figure 1. Spherical electrode geometry.



||||
 x_j

This work was supported in part by a grant from the
Office of Naval Research, Washington, D.C.

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	<u>No. Copies</u>		<u>No. Copies</u>
Office of Naval Research Attn: Code 472 800 North Quincy Street Arlington, Virginia 22217	2	U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 1211 Research Triangle Park, N.C. 27709	1
ONR Branch Office Attn: Dr. George Sandoz 536 S. Clark Street Chicago, Illinois 60605	1	Naval Ocean Systems Center Attn: Mr. Joe McCartney San Diego, California 92152	1
ONR Area Office Attn: Scientific Dept. 715 Broadway New York, New York 10003	1	Naval Weapons Center Attn: Dr. A. B. Amster, Chemistry Division China Lake, California 93555	1
ONR Western Regional Office 1030 East Green Street Pasadena, California 91106	1	Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko Port Hueneme, California 93401	1
ONR Eastern/Central Regional Office Attn: Dr. L. H. Peebles Building 114, Section D 666 Summer Street Boston, Massachusetts 02210	1	Department of Physics & Chemistry Naval Postgraduate School Monterey, California 93940	1
Director, Naval Research Laboratory Attn: Code 6100 Washington, D.C. 20390	1	Dr. A. L. Slafkosky Scientific Advisor Commandant of the Marine Corps (Code RD-1) Washington, D.C. 20380	1
The Assistant Secretary of the Navy (RE&S) Department of the Navy Room 4E736, Pentagon Washington, D.C. 20350	1	Office of Naval Research Attn: Dr. Richard S. Miller 800 N. Quincy Street Arlington, Virginia 22217	1
Commander, Naval Air Systems Command Attn: Code 310C (H. Rosenwasser) Department of the Navy Washington, D.C. 20360	1	Naval Ship Research and Development Center Attn: Dr. G. Bosmajian, Applied Chemistry Division Annapolis, Maryland 21401	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12	Naval Ocean Systems Center Attn: Dr. S. Yamamoto, Marine Sciences Division San Diego, California 91232	1
Dr. Fred Saalfeld Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375	1	Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1

SP472-3/A3

472:GAN:716:ddc
78u472-608

TECHNICAL REPORT DISTRIBUTION LIST, GEN

No.
Copies

Dr. Rudolph J. Marcus
Office of Naval Research
Scientific Liaison Group
American Embassy
APO San Francisco 96503

1

Mr. James Kelley
DTNSRDC Code 2803
Annapolis, Maryland 21402

1

TECHNICAL REPORT DISTRIBUTION LIST, 359

	<u>No. Copies</u>		<u>No. Copies</u>
Dr. Paul Delahay Department of Chemistry New York University New York, New York 10003	1	Dr. P. J. Hendra Department of Chemistry University of Southampton Southampton SO9 5NH United Kingdom	1
Dr. E. Yeager Department of Chemistry Case Western Reserve University Cleveland, Ohio 41106	1	Dr. Sam Perone Department of Chemistry Purdue University West Lafayette, Indiana 47907	1
Dr. D. N. Bennion Department of Chemical Engineering Brigham Young University Provo, Utah 84602	1	Dr. Royce W. Murray Department of Chemistry University of North Carolina Chapel Hill, North Carolina 27514	1
Dr. R. A. Marcus Department of Chemistry California Institute of Technology Pasadena, California 91125	1	Naval Ocean Systems Center Attn: Technical Library San Diego, California 92152	1
Dr. J. J. Auborn Bell Laboratories Murray Hill, New Jersey 07974	1	Dr. C. E. Mueller The Electrochemistry Branch Materials Division, Research & Technology Department Naval Surface Weapons Center White Oak Laboratory Silver Spring, Maryland 20910	1
Dr. Adam Heller Bell Laboratories Murray Hill, New Jersey 07974	1	Dr. G. Goodman Globe-Union Incorporated 5757 North Green Bay Avenue Milwaukee, Wisconsin 53201	1
Dr. T. Katan Lockheed Missiles & Space Co, Inc. P.O. Box 504 Sunnyvale, California 94088	1	Dr. J. Boechler Electrochimica Corporation Attention: Technical Library 2485 Charleston Road Mountain View, California 94040	1
Dr. Joseph Singer, Code 302-1 NASA-Lewis 21000 Brookpark Road Cleveland, Ohio 44135	1	Dr. P. P. Schmidt Department of Chemistry Oakland University Rochester, Michigan 48063	1
Dr. B. Brummer EIC Incorporated 55 Chapel Street Newton, Massachusetts 02158	1	Dr. H. Richtol Chemistry Department Rensselaer Polytechnic Institute Troy, New York 12181	1
Library P. R. Mallory and Company, Inc. Northwest Industrial Park Burlington, Massachusetts 01803	1		

TECHNICAL REPORT DISTRIBUTION LIST, 359

	<u>No. Copies</u>		<u>No. Copies</u>
Dr. A. B. Ellis Chemistry Department University of Wisconsin Madison, Wisconsin 53706	1	Dr. R. P. Van Duyne Department of Chemistry Northwestern University Evanston, Illinois 60201	1
Dr. M. Wrighton Chemistry Department Massachusetts Institute of Technology Cambridge, Massachusetts 02139	1	Dr. B. Stanley Pons Department of Chemistry University of Alberta Edmonton, Alberta CANADA T6C 2G2	1
Larry E. Plew Naval Weapons Support Center Code 30736, Building 2906 Crane, Indiana 47522	1	Dr. Michael J. Weaver Department of Chemistry Michigan State University East Lansing, Michigan 48824	1
S. Rubv DOE (STOR) 600 E Street Washington, D.C. 20545	1	Dr. R. David Rauh EIC Corporation 55 Chapel Street Newton, Massachusetts 02158	1
Dr. Aaron Wold Brown University Department of Chemistry Providence, Rhode Island 02192	1	Dr. J. David Margerum Research Laboratories Division Hughes Aircraft Company 3011 Malibu Canyon Road Malibu, California 90265	1
Dr. R. C. Chudacek McGraw-Edison Company Edison Battery Division Post Office Box 28 Bloomfield, New Jersey 07003	1	Dr. Martin Fleischmann Department of Chemistry University of Southampton Southampton 509 5NH England	1
Dr. A. J. Bard University of Texas Department of Chemistry Austin, Texas 78712	1	Dr. Janet Osteryoung Department of Chemistry State University of New York at Buffalo Buffalo, New York 14214	1
Dr. M. M. Nicholson Electronics Research Center Rockwell International 3370 Miraloma Avenue Anaheim, California	1	Dr. R. A. Osteryoung Department of Chemistry State University of New York at Buffalo Buffalo, New York 14214	1
Dr. Donald W. Ernst Naval Surface Weapons Center Code R-33 White Oak Laboratory Silver Spring, Maryland 20910	1	Mr. James R. Moden Naval Underwater Systems Center Code 3632 Newport, Rhode Island 02840	1

TECHNICAL REPORT DISTRIBUTION LIST, 359

	<u>No. Copies</u>		<u>No. Copies</u>
Dr. R. Nowak Naval Research Laboratory Code 6130 Washington, D.C. 20375	1	Dr. John Kincaid Department of the Navy Statagic Systems Project Office Room 901 Washington, DC 20376	1
Dr. John F. Houlihan Shenango Valley Campus Pennsylvania State University Sharon, Pennsylvania 16146	1	M. L. Robertson Manager, Electrochemical Power Sonices Division Naval Weapons Support Center Crane, Indiana 47522	1
Dr. M. G. Sceats Department of Chemistry University of Rochester Rochester, New York 14627	1	Dr. Elton Cairns Energy & Environment Division Lawrence Berkeley Laboratory University of California Berkeley, California 94720	1
Dr. D. F. Shriver Department of Chemistry Northwestern University Evanston, Illinois 60201	1	Dr. Bernard Spielvogel U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709	1
Dr. D. H. Whitmore Department of Materials Science Northwestern University Evanston, Illinois 60201	1	Dr. Denton Elliott Air Force Office of Scientific Research Bldg. 104 Bolling AFB Washington, DC 20332	1
Dr. Alan Bewick Department of Chemistry The University Southampton, SO9 5NH England	1		
Dr. A. Himy NAVSEA-5433 NC #4 2541 Jefferson Davis Highway Arlington, Virginia 20362	1		

DA
FILM